

Testing entropy production hypotheses in non-linear steady states

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Abstract

In the last few decades, some hypotheses for entropy production (EP) principles have been forwarded as possible candidates for organizational principles in non-linear non- equilibrium systems. Two important hypotheses will be studied: the maximum entropy production (MaxEP) principle that claims that the selected steady state has the highest EP, and the gradient response principle that claims that the EP of the selected steady state (maximally) increases when the external thermodynamic driving force increases. We will formulate these hypotheses more rigorously and present a simple chemical reaction model to test these hypotheses. With the help of this model, we will clearly demonstrate that there are different MaxEP hypotheses being discussed in the literature and we will look at some parts in the literature where these differences are not always clarified. Furthermore, our chemical model will be a general counter example to all of these MaxEP and gradient response hypotheses.

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1 Introduction

In the linear response regime near thermodynamic equilibrium, it is well known that one can derive constitutive equations of motion by using a variational principle of least dissipation (Onsager, [17, 18]), and one can find the unique steady state by minimizing the entropy production (MinEP) under some physical constraints (as first discussed by Prigogine [25, 10]). By using other constraints, one can find respectively the constitutive equations of motion and the steady state by maximizing the entropy production (MaxEP, see resp. [35] and [36, 37]).

The situation far from thermodynamic equilibrium, with nonlinear dynamics and non-linear response, is much more difficult. Far from equilibrium not only involves thermodynamic constraints, but the description is also highly dependent on the kinetics (the balance or constitutive equations). Entropy production (EP) is a fundamental notion in irreversible thermodynamics, because it combines entropy (thermodynamics) with time (kinetics), it is tempting to look for EP principles. Besides successes of the near-equilibrium (linear response) MinEP and MaxEP, there is also some renewed interest in a non-linear MaxEP, for systems far from equilibrium² (see e.g. [9]), from complex chemical reaction

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²With systems far from equilibrium, we mean systems in local equilibrium, but not in the linear response regime. Although (non-) linear response is not equivalent with (non-) linear dynamics, the referred studies as well as the model in this article are non-linear in both meanings.

systems [7] to fluid systems [31] or even ecological [8] and climate systems [21]. Recent reviews include [13] and [19].

Schneider et al. [29] also formulated another EP hypothesis, which we will call the gradient response principle. The above MinEP and MaxEP principles are formulated for a fixed external thermodynamic driving force (external applied gradient), whereas the gradient response studies the behavior of the EP in the selected steady state, when the external gradient increases. The intuition behind this principle is that when systems are pushed further away from equilibrium, they will try harder to get to equilibrium. As the external applied gradient is a measure for the distance from equilibrium and the EP is a measure for how strong the system tends to equilibrium, the gradient response hypothesis roughly states that the steady state EP (maximally) increases when the external applied gradient increases.

In this article, a chemical reaction model is presented, which is inspired by a resource-consumer-predator system in ecology. The system's EP properties in the steady states are studied, and it is used to test the EP hypotheses. With this model we can easily demonstrate that there are actually different MaxEP principles in use in the literature. Apart from the distinction between linear and non-linear principles, one can make a distinction between steady state principles and transient principles. The latter principles are used e.g. to derive constitutive equations of motion which are valid in both the transient and the steady states. An example is Onsager's least dissipation [17, 18]. Also Prigogine's MinEP principle [25] compares the steady state EP with the EP in the neighboring transient states. The latter principle (not to be confused with Onsager's) can also be called a Lyapunov principle because in this principle the EP is mathematically a Lyapunov functional [10].

We will only examine the steady state non-Lyapunov principles, which we have named the partial steady state MaxEP, the non-variational MaxEP and the maximum gradient response for reasons that will become clear later. Some parts in the literature where these differences between MaxEP principles are not clarified, will be mentioned in the final discussion section. These non-linear MaxEP principles are also very different from the linear MaxEP principles [35, 36, 37] (which are basically correct in the linear response regime).

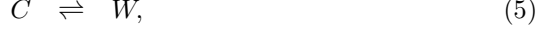
Apart from pointing at these differences between MaxEP principle, a second important result is that this one chemical reaction model might serve as a general counter example to all of these most used MaxEP hypotheses (although some hypotheses have much simpler counter examples). The author is not aware of real systems obeying the same dynamics, and therefore references to experimental studies will not be made. From a theoretical point of view, the model is consistent and obeys all known physical laws. It is not more complex than e.g. the Belousov-Zhabotinsky system [10]. If nature in reality excludes all counter example systems, this would be a new physical law.

2 The chemical reaction model

2.1 General description

Let us study the entropy production in a specific chemical reaction system. The system consists of five chemical substances A , R , C , P and W . The reaction

set has six reactions



The concentrations will be denoted with the same letters. The concentrations A and W are kept fixed. This reaction scheme is well known and much studied in ecology as a description for a resource-consumer-predator ecosystem [14], whereby A and R represent the resource, C is the primary consumer, P is the (omnivore) predator and W is the dead organic waste.

Each reaction has a rate F_i ($i = 1, \dots, 6$), and they determine the dynamical equations. We will take them as simple as possible, but still physically realistic:

$$\frac{dR}{dt} = f_{AR}A - b_{AR}R - 2f_{RC}RC - 2f_{RP}RP, \quad (7)$$

$$\frac{dC}{dt} = f_{RC}RC - 2f_{CP}CP - f_C C, \quad (8)$$

$$\frac{dP}{dt} = f_{RP}RP + f_{CP}CP - f_P P. \quad (9)$$

We have neglected the (backward rate) terms in W because this concentration is assumed to be very small.

The thermodynamic forces X_i for each reaction are given by the affinities, the sum of the chemical potentials, weighted by their stoichiometric coefficients [10]. For ideal gases or ideal and perfect solutions, the chemical potentials are (up to constants) given by the logarithm of the concentrations. We will only need the following overall affinities:

$$X_{AW} = \mu_A - \mu_W = \ln \frac{K_{AW}A}{W}, \quad (10)$$

$$X_{AR} = \mu_A - \mu_R = \ln \frac{K_{AR}A}{R}, \quad (11)$$

$$X_{RW} = \mu_R - \mu_W = \ln \frac{K_{RW}R}{W}, \quad (12)$$

with $X_{AR} + X_{RW} = X_{AW}$ the total, external driving force (applied gradient), which is fixed. The latter equation leads to the relation $K_{AW} = K_{AR}K_{RW}$ between the equilibrium constants. Note that the W can not be neglected in the logarithms and that for simplicity we have neglected the absolute temperature factor in front of the logarithm.

The total EP can be written as the sum of the six terms $\sigma_{tot} = \sum_i F_i X_i$. After some calculations and some thermodynamic consistency equations (basically Hess's law, see e.g. [10]) one can write down a very simple expression for the total steady state EP (the steady states are denoted with upperindex γ):

$$\sigma_{tot}^\gamma = (f_{AR}A - b_{AR}R^\gamma) \ln \frac{K_{AW}A}{W}. \quad (13)$$

This can be understood by observing that there is no net accumulation of R , C or P , and therefore the overall reaction rate from A to W is $f_{AR}A - b_{AR}R^\gamma$. This should be multiplied with the overall force X_{AW} .

Next, we have to solve the dynamics, find the steady states (especially R^γ), and determine the asymptotic stability. The dynamics looks like a resource-consumer-omnivore ecosystem model, whose steady states and stability were calculated in [14].

We will not present the expressions for the steady states here, but we will immediately present a qualitative picture (by taking the parameter values as e.g. $f_{AR} = b_{AR} = f_{CP} = f_C = 1$, $f_P = f_{RC} = f_{RP} = 2$, and doing some rescaling to make things more visible) of the total steady state EP in Fig. 1. As the overall constant driving force X_{AW} is an increasing function of the parameter A (for constant and very small W), it is sufficient to express the EP as a function of A . Only the realistic steady states are shown; there are other unphysical states with (very small) negative concentrations. Calculating the stability is simply done by looking at the eigenvalues of the dynamical system linearized around the steady state. There are two saddle-node (fold) bifurcations at A_{III} and A_{IV} . The states indicated by 'c' and 'd' are on the stable branches, but when they get close to the saddle-node points, their linear stability decreases. Therefore, by taking them sufficiently close to the saddle-nodes, they have a lower stability than the states 'a' and 'e' which are further away from the saddle-nodes. This remark will become important in our later discussions.

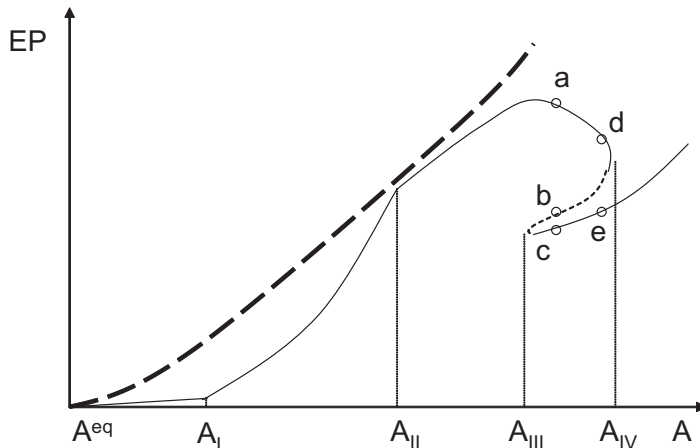


Figure 1: A qualitative picture of the EP in the steady states as a function of A . The thick dashed line is the EP obtained from the partial steady state MaxEP principle. The thin solid lines are the EP in the asymptotically stable steady states. The thin dotted line consists of the unstable states.

With this set-up, we can look at MaxEP. We will see that there are different MaxEP principles. These differences will become clear by using our chemical reaction example.

2.2 Partial steady state MaxEP

The work by Paltridge [21, 22, 23] to understand the convective heat flows in the earth atmosphere was a starting point to study maximum entropy production in highly non-linear systems. The basic idea behind the Paltridge model is rather simple. The atmosphere is divided in two compartments, the equator and the poles, and only the energy balance in the atmosphere is considered. Solar energy is irradiated at the equator. There is an atmospheric (and oceanic) heat flux from the equator to the poles, where the energy is reradiated back into space. All the processes can be split into 'simple' or linear and 'complex' or non-linear ones. In the Paltridge model, the simple processes are basically the radiation processes, the complex processes are the heat transport processes by fluid convection from equator to pole. The non-linear highly complex atmosphere subsystem is regarded as a black box, without knowing the exact internal dynamics. MaxEP claims that the heat transport coefficient of the atmosphere, the heat flow from equator to pole, and the driving force (the temperature gradient) on earth will settle themselves in a state of maximum atmospheric EP. This partial steady MaxEP approach has been made more precise and extended to study atmospheres of other planets [6, 9, 11, 16, 19, 34]. The derived values for the steady state heat transport coefficient are consistent with a number of experiments.

Remarkably, this MaxEP principle was later on also applied to other physical systems, like electric arcs [1], photosynthetic [7] or ATP synthase [5] chemical reactions. In these chemical reaction system, there were again 'simple' and 'complex' reactions. The 'complex' chemical reaction rate parameters (e.g. the parameters regulating the transition $P.ADP \rightleftharpoons ATP$ in [5]) were derived by postulating MaxEP, and these obtained values were also compatible with experimental data.

Stated generally, the partial steady state MaxEP principle states that the EP in the steady state of only the complex non-linear processes, i.e. a *partial* EP (not the total EP of all processes), is maximized with respect to a continuous 'effective' parameter (e.g. the effective atmospheric heat transport or the reaction rate parameter) or 'effective' flux related with those complex processes.

To make the procedure more clear, let us apply this partial steady state MaxEP principle to our model. As can be seen, $F_{AR} = f_{AR}A - b_{AR}R$ is a 'simple' linear expression. The non-linearities occur in the flow from R to W . First we will describe the latter flow as a 'black box', without specifying the internal dynamics. Afterwards, we will compare the obtained MaxEP result with the internal dynamics (7-9).

Suppose the system selects a steady state, which we will write with an upper-index *. The MaxEP principle claims that this selected state is the one which has a maximum EP for the non-linear processes. These processes can be grouped in an 'effective' flux $F_{RW}^* = f_{RW}R^*$ from R to W (again the term containing W is neglected in the flux expression), with f_{RW} the 'effective' parameter. The non-linear part of the EP is given by

$$\sigma_{RW}^* = F_{RW}^* X_{RW}^* \quad (14)$$

$$= F_{RW}^* \ln \frac{K_{RW} R^*}{W} \quad (15)$$

$$= F_{RW}^* \ln \frac{K_{RW}(K_{AR}A - F_{RW}^*/b_{AR})}{W}, \quad (16)$$

with $0 \leq F_{RW}^* \leq K_{AR}b_{AR}A$. We have used the steady state constraint $F_{RW}^* = f_{AR}A - b_{AR}R^*$ and $K_{AR} = f_{AR}/b_{AR}$.

As one can see, in the above expression there is a trade-off between F_{RW}^* and X_{RW}^* . As the former increases, the latter decreases, and vice versa. Therefore, there is an optimal value for F_{RW}^* . Taking the maximum of this EP with respect to F_{RW}^* , one finds

$$F_{RW,MaxEP}^* = \frac{(\mathbf{Lw}(K_{AW}Ae/W) - 1) K_{AR}b_{AR}A}{\mathbf{Lw}(K_{AW}Ae/W)} \quad (17)$$

with \mathbf{Lw} the LambertW function and e Euler's number. The above expression gives F_{RW}^* as a function of A (at constant and very small W).

With this expression we can calculate R_{MaxEP}^* and the total EP, which is indicated in Fig. 1. Let us now compare this result with the EP obtained from the specified internal dynamics (7-9). It is clear that this does not correspond with the EP's in the stable steady states by directly solving the concrete dynamics. We can conclude that the partial steady state MaxEP principle does not hold in our example.

There is a difference between the atmospheric system and our chemical system. The atmosphere is highly non-linear and has a lot of possible processes and degrees of freedom. One can argue that even though our chemical system is non-linear, it is not 'non-linear enough', or it does not have enough degrees of freedom (we have basically only three macroscopic variables: R , C and P). Keeping the successes of equilibrium thermodynamics in mind, some intuition might indicate that a similar kind of 'law of large numbers' can be applied in non-equilibrium complex systems, resulting in MaxEP. However, it is not clear why adding macroscopic variables or other non-linear terms should result in the correct flow $F_{RW,MaxEP}^*$. The steady state solutions remain sensitive on the parameter values. To explain the experimental successes of MaxEP in e.g. atmospheric models, one needs to know what kind of properties are required for the internal dynamics in order to obtain the correct MaxEP state.

2.3 Non-variational MaxEP

It is very often claimed [13, 28, 30, 32] that an isolated non-equilibrium system relaxes to equilibrium 'as fast as possible', that it 'follows the most efficient route' to increase its entropy [33] or that it 'selects the path' with highest EP. The idea behind this is that a non-equilibrium system is in a small region in phase space with low entropy, and has the highest probability to evolve in the next time step to the largest region, with highest entropy. These statements are still quite vague, and it is not clear what kind of constraints are involved.

One can try to make the above formulations a bit more precise. First we have to make the notion of 'paths' more precise. Let us restrict the 'paths' to (pseudo) steady states: Suppose there are different paths, i.e. steady states, then the steady state with highest EP, i.e. the one moving to equilibrium as fast as possible, will be 'selected'. Secondly we have to make the notion 'select' more precise. The real steady state that is selected can be the one that is e.g. the most stable. There are many notions of stability. Let us take asymptotic (linear) stability. The reformulation reads: 'The steady state with highest EP is the most asymptotically stable.' Mathematically, this means that when the

dynamics are highly non-linear, then they might lead to different steady states M^γ ($M = A, R, \dots, W$) and $X_i^\gamma(M^\gamma)$, $F_i^\gamma(M^\gamma)$. Denote with upper index $\gamma = *$ the most asymptotically stable state. Then the claim is

$$\sigma^*(X^*, F^*) \geq \sigma^\gamma(X^\gamma, F^\gamma), \quad \forall \gamma. \quad (18)$$

An important remark is that this principle is not a variational principle, because there is no action and no variation with respect to continuous variables (such as fluxes) or 'effective' parameters. It is rather a selection principle of a discrete number of steady states. In this sense, it is from a very different nature than the non-linear partial steady state MaxEP.

This non-variational MaxEP principle is also related to the notion of dissipative systems with dissipative structures. If one drives the system out of equilibrium, at certain critical levels of the driving force, bifurcations to other stable states are possible. Then a patterned or ordered structure might arise. A famous example is the Rayleigh- Bénard system [26]. This consists of a viscous fluid subject to a gravitating field and a temperature gradient: The bottom layer is heated whereas the upper is cooled. At a critical level of the temperature gradient, the heat-conducting state is transformed to a heat- convecting state, with convection cells in a regular pattern, called the dissipative structure. The claim is that this ordered dissipative structure (if it exists) always has a higher EP than the so called 'thermodynamic branch' state without the structure, i.e. the state, like the conduction state, which do not show a pattern.

There is some verification of this principle from a number of studies. The most important field to study this principle is fluid dynamics. Shimokawa et al. [20, 31], based on work by e.g. Malkus [12], studied turbulent and (oceanic) fluid systems, and they discovered that the MaxEP state is most stable against perturbations. Also Schneider et al. [29] describe the increase in EP when the Bénard fluid system moves to the stable convection state. Rennó [27] suggested that the most stable state in a radiative-convective atmosphere model with two stable states has the highest EP. Also in the Brusselator chemical reaction system, non-variational MaxEP was observed with numerical simulations (see Sawada [28], although Sawada termed it perhaps confusingly a variational principle, although there was not a clear notion of an action presented.)

Other studies showed possible counterexamples to the non-variational MaxEP principle. When the external driving force parameter increases, bifurcations towards new patterns and dissipative structures might occur. Most of the above mentioned studies were restricted to the dissipative structures after the first bifurcation (e.g. the transition from the conduction to the convection state). However, when the system is pushed further out of equilibrium, new bifurcations might arise, resulting into new stable states and patterns. The old states become unstable. And as is shown by numerical simulations [2, 3, 15], the total heat transport and EP of these new states might be *lower* as compared with the unstable states. (Nicolis [15] also gave a counterexample of the non-variational MaxEP principle for chemical reactions.)

These numerical counterexamples were criticized by Martyuchev et. al. [13] by claiming that there are computational difficulties involved, that the criteria of stability and coexistence in numerical simulations are subjective, and that taking time-averages or spatial integrations are dubious. Our chemical reaction model can serve as a simple counterexample for the non-variational MaxEP

principle, without the need for computer simulations because it is analytically solvable. Hence the above criticism does not apply to our case.

Let us go to our model. As can be seen in Fig. 1, there are two critical levels A_I and A_{II} , with sharp changes in the EP. The behavior near A_I is analogous to the bifurcation behavior in the Rayleigh-Bénard convection system, switching from the conduction state (for $A < A_I$) to the convection state (when $A > A_I$). The interesting property of our chemical reaction system is that we can easily look what happens after a second bifurcation at A_{II} , without the need for numerical simulations. As discussed above, the state corresponding with 'd' in Fig. 1 is *less* stable but has a *higher* EP than the state in 'e': $\sigma^d > \sigma^e$. This counters the non-variational MaxEP hypothesis.

This counterexample was perhaps already hinted at by Sawada [28], who claimed that the non-variational MaxEP could be wrong in the presence of hysteresis. Nevertheless, there are still the numerical Rayleigh-Bénard system simulations without non-variational MaxEP and without hysteresis [2].

2.4 Maximum gradient response

Schneider and Kay [29] studied the degradation of an externally applied gradient. This gradient is the external driving force, and its degradation means an EP. Schneider and Kay looked at the change in EP when the external driving force is increased. They formulated what they have called a 'restated second law of thermodynamics'.

"The thermodynamic principle which governs the behavior of systems is that, as they are moved away from equilibrium, they will utilize all avenues available to counter the applied gradients. As the applied gradients increase, so does the system's ability to oppose further movement from equilibrium."

We have called this principle the maximum gradient response. It needs some further specification, because it is still quite vague.

We can give at least three different interpretations. These interpretations are formulated as: In the most asymptotically stable state

- the EP is positive.
- the EP is increasing as the gradient increases.
- the EP is increasing and it is a steeper function compared with the EP of the less stable steady states.

The first of the above statements is nothing but the second law. The latter two statements are a weaker and a stronger extension. Our model can serve as a counterexample of these latter two statements.

As mentioned, the state 'a' in Fig. 1 is more asymptotically stable than 'b' (which is unstable) or 'c'. However, $\frac{d\sigma^a}{dA} \leq 0$ and $\frac{d\sigma^b}{dA} > \frac{d\sigma^c}{dA}$. So the most stable steady state is not always increasing, nor is it the steepest.

Related with this gradient response principle, Woo [33] discussed the behavior under pseudo-stationarity conditions: When the external reservoirs (corresponding with A and W) are very large but finite, the concentrations A and W are not fixed but they are very slowly relaxing towards equilibrium. It was claimed that $\frac{d\sigma^*}{d\tau} \leq 0$, with τ the time corresponding with the time scale of this relaxation process. This relaxation is basically a slow movement towards the equilibrium value $A^{eq} = W/K_{AW}$ far left in the Fig. 1. However, a movement from 'd' to 'a' is possible, leading to an *increase* in EP, instead of a decrease. Even sudden decreasing or increasing jumps are possible when A is varied.

3 Further discussion

As we have seen, our chemical reaction model clearly shows a counter argument for MaxEP. Looking at Fig. 1, one can argue that 'anything goes' for the EP, except that the specific EP for every independent reaction is positive.

But what we can also remark, is that there is not one MaxEP principle, but there are different principles, having very different descriptions. The distinctions between these MaxEP principles, especially between the partial steady state MaxEP and the non-variational MaxEP, are not always clear in the literature. We will briefly discuss some of these shortcomings in the literature.

In [33], the non-variational MaxEP is misleadingly related with a variational principle, the least dissipation. The latter principle by [17] is only valid near equilibrium, i.e. in the linear response regime. The possibility for a non-linear least dissipation principle is still unknown. Nevertheless, the connection in [33] between a variational and a non-variational principle was proposed, without stressing its differences.

Also in e.g. Dewar [4] and Ozawa et al. [20], as well as in some reviews [13] and [19], both the partial steady state and non-variational principles are discussed without stressing their differences. The discussion of the partial steady state principle is mostly done by using the atmospheric climate system, whereas the discussion of the non-variational principle mostly uses the Rayleigh-Bénard convection system. However, as we have seen, these principles are very different, because for example there is no guarantee that the most stable state (with highest total EP) has the correct value for some transport coefficient (e.g. the heat flow rate in the atmosphere, or a chemical reaction rate) such that the partial EP related with this transport is maximal.

One can also see the difference between partial steady state and non-variational MaxEP as follows. The non-variational MaxEP uses the total steady state EP. This can be written as $\sigma^* = \bar{X}F^*$ with \bar{X} the constant overall force (e.g. the fixed boundary temperature difference in the Rayleigh-Bénard system, or the fixed chemical potential difference in the chemical reaction system). Suppose we want to find the unknown total flux F^* by extremizing the corresponding total EP. However, this would be a meaningless operation, because it would result in an infinity. We did not encounter this infinity in the partial steady state MaxEP example discussed in section 2.2, because this principle did not use to the total EP, but a partial EP instead. For the partial EP related with the non-linear processes, there is a trade-off. One could have a non-fixed X_k^* which might decrease when F_k^* increases. Hence, due to this trade-off one avoids meaningless infinities.

Another point of discussion is the relation of the partial steady state MaxEP principle with a transient (Lyapunov) principle. If the relaxation of the transient states towards the steady state is such that the specific EP behaves as $\frac{d\sigma_{RW}}{dt} \geq 0$, reaching its maximum in the selected steady state, then the partial steady state MaxEP is a Lyapunov principle. It is an open question whether the examples of the partial steady state MaxEP principle discussed in the literature have a Lyapunov-type behavior.

As we have presented a general counter example, this does not totally degrade the value of MaxEP. The non-linear partial steady state MaxEP might be wrong in most interesting cases (such as turbulent fluid flows [2]), but on the other hand, the partial steady state principle has some experimental strength

[11] (see [19] for review). The latter principle is not trivial, and its experimental verification specifically comes from interesting systems, such as turbulent atmospheric and ocean systems. This experimental corroboration needs some explanation. If one could find a non-trivial theoretical model (an attempt was made in e.g. [24]) that shows this partial steady state MaxEP, this might increase our understanding of some highly non-linear systems.

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